Kinetics and Catalysis, Vol. 44, No. 6, 2003, pp. 866–869. Translated from Kinetika i Kataliz, Vol. 44, No. 6, 2003, pp. 943–947.

CHRONICLE

Advances in the Understanding and Application of Catalysts (Russian–American Seminar on Catalysis, Moscow, May 28–30, 2003)

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Received June 9, 2003

On May 28–30, 2003, the Russian–American Seminar “Advances in the Understanding and Application of Catalysts” was held in Moscow. The organizers of this meeting were the Boreskov Institute of Catalysis (Russian Academy of Sciences, Novosibirsk, Russia) and the University of California (Berkeley, USA). About 90 researchers, including 7 from the United States, took part in the seminar. Most of Russian participants were from Novosibirsk and Moscow.

The seminar was held after a long break in relations between researchers from USSR/Russia and the United States. In the 1970s, according to the Brezhnev–Nixon agreement, cooperative research program on chemical catalysis was established. Annual joint seminars on catalysis have been held in turns in the United States and in the Soviet Union. Three seminars were held in Moscow, Novosibirsk, and Kiev and three others were held in Princeton, Aspen, and Cherry Hill. Up to 10–15 professors from each country had been visiting catalytic laboratories abroad for 6–10 months. Cooperation was successful. Unfortunately it was discontinued in 1980, by then US President J. Carter, when Russian troops entered Afghanistan. One more Russian–American seminar devoted to the problems of environmental catalysis and organized by DuPont was held in 1992 in Wilmington (Delaware, USA).

The 2003 Moscow seminar consisted of seven plenary lectures, 32 oral talks, and approximately 50 posters. Most of the contributions were from the Boreskov Institute of Catalysis: 2 plenary lectures, 13 oral talks, and 21 posters. Most of talks were devoted to the mechanism of catalysis, applications of *in situ* techniques, and catalyst structures. This review considers mostly plenary lectures and oral talks.

NEW METHODS OF STUDIES

The lecture by Professor A. Bell (UC, Berkeley) was devoted to the EXAFS study of the local structure of iron atoms in FeZSM-5. Iron atoms were shown to exist as isolated cations rather than paired centers as suggested in the literature. These cations have a tetrahedral environment and the Fe–Al coordination number is close to unity regardless of the Fe/Al ratio. This structure essentially does not change upon treatment in an atmosphere of He or CO. Iron has a similar structure in silicalite.

In another one of Bell’s talk,[1] the UV–VIS spectroscopic study of the mechanism of propane oxidative dehydrogenation over supported vanadium catalysts was discussed. The authors showed that in the region of pre-edge absorbance, the spectrum intensity is strictly proportional to the concentration of the reduced forms of vanadium. This fact made it possible to study the processes of reduction and oxidation of the catalyst under conditions of oxidative dehydrogenation of propane.

V.I. Bukhtiyarov (Boreskov Institute of Catalysis) presented a comprehensive review of the application of various physical methods. The author presented his own and literature data obtained by the known methods (IRAS and XANES) and by the new methods: sum frequency generation (SFG) and polarization modulation infrared absorption spectra (PM IRAS). New methods require sophisticated equipment and in some cases synchrotron radiation sources. Therefore, they are only used in few laboratories worldwide. Applications of these methods under conditions of catalysis were reported. Specifically, the author’s research into CO adsorption and CH_3OH decomposition on Pd(111) and the partial oxidation of methanol to formaldehyde on copper was reported. These methods can be applied at pressures of 10–20 Torr and in principle can be used in kinetic studies, although there are some difficulties with low sensitivity.

I.I. Ivanova (Department of Chemistry, Moscow State University) presented an analogous lecture. She presented a review of the current state and prospects in application of MAS NMR in heterogeneous catalysis. Special attention was given to experimental capabilities of this method for studying a catalytic process in a flow-type reactor. Examples are given of NMR applications in the mechanistic studies of reactions of olefins, alkanes, alcohols, aromatics, and halogenated compounds. The NMR method is very informative, but it has been applied in most cases to the studies of catalytic reactions over zeolites. This is largely due to the fact that, in the case of zeolites, high concentrations of inter-

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[1] Henceforth, the presenting author is mentioned.

mediate products are reachable in a measurement cell. A drawback of the method is that the instrument is expensive: an NMR spectrometer is two times more expensive than an IR spectrometer.

I.V. Koptyug (Boreskov Institute of Catalysis) applied *in situ* NMR to obtain the microimage of the liquid phase participating in the catalysis and located inside the catalyst pellets and in the bed of catalyst grains. The following reactions were studied: α-methylstyrene hydrogenation, H_2O_2 decomposition, and the Belousov–Zhabotinskii reaction in the liquid phase and in the presence of a solid inert bed. In the case of α-methylstyrene hydrogenation, the liquid phase exfoliates into domains of two types with different contents of the liquid phase. In the case of H_2O_2 decomposition, the existence of the convective flow along the catalyst grains exists. In the Belousov–Zhabotinskii reaction, chemical waves in the bed of granulated catalyst were found.

NEW CATALYSTS AND CATALYTIC REACTIONS

Several lectures and reports presented data on new catalysts and new reactions. Partial oxidation of alkanes attracts broad attention worldwide. V.V. Guliants (University of Cincinnati, USA) reported in his lecture the development of a new active and selective mixed metal oxide catalyst Mo–V–Te–O for the direct oxidation of propane to acrylic acid with a selectivity of 70–80%. Analogous catalysts have already been applied to propylene oxidation to acrylic acid. The structure and the phase composition of the catalyst and the roles of phases in the process were considered.

In another report, Guliants described a collaborative study with Dipartimento di Chimica Industriale e dei Materiali (Bologna, Italy) of new mesoporous molecular sieves of the M41S family. The addition of Mo and V atoms makes these materials catalytically active. Recently, a mesostructured thermally stable vanadyl phosphate, applicable as a partial oxidation catalyst for *n*-butane conversion into maleic anhydride, has been synthesized. A multicomponent mesophase Mo–V–M–O (M = Nb, Te) catalyst for the selective oxidation of propane to propylene and oxygenates was also reported.

G.I. Panov (Boreskov Institute of Catalysis) continued his study on the partial oxidation of hydrocarbons by N_2O. These studies have begun with the discovery of the unique property of the zeolite to catalyze the selective oxidation of benzene to phenol. This process reached the state of a large-scale production unit. Then, the oxidation of other aromatic compounds (toluene and naphthalene) into the corresponding compounds was studied. Recently, it was discovered that N_2O can oxidize unsaturated compounds in a liquid phase without a catalyst. Oxidation occurs due to the interaction of N_2O with C=C bonds, forming carbonyl compounds.

According to the author, N_2O is a more expensive oxidant than molecular oxygen, but it is cheaper than H_2O_2. In another contribution from the Boreskov Institute (A.S. Noskov *et al.*), the development of large-scale (50000–100000 ton per year) N_2O production by ammonia oxidation was considered. The maximal selectivity was 90% and the conversion of ammonia was almost complete over a Mn–Bi–O catalyst at 330–370°C. The use of a fluidized bed reactor allowed the authors to use concentrations of ammonia as high as 50%.

G.M. Zhidomirov (Boreskov Institute of Catalysis and Eindhoven University of Technology, Netherlands) reported a DFT study of intermediate substances in the oxidation of benzene to phenol by N_2O on FeZSM-5. The interaction of the active site OFe/Z (α-oxygen) with benzene leads to the formation of an arene oxide with a low activation energy. Intermediate ions, phenol keto tautomer, and phenol are then formed. The rate-limiting step of the reaction is the transformation of arene oxide into a zwitterion.

One of the interesting discoveries in catalytic oxidation is the partial oxidation by a mixture of H_2 and O_2. The $OH^{\bullet}$ radicals or hydrogen peroxide formed in the course of a process make it possible to carry out the selective hydroxylation at a rather low temperature. A.V. Kalinkin (Boreskov Institute of Catalysis) and D.W. Goodman (Texas A&M University, USA) studied the interaction of pure H_2 and the $H_2 + O_2$ mixture with the model $Pt/MoO_3/Mo$ catalysts. It was shown that platinum accelerates molybdenum reduction.

I.N. Zavalishin (Topchiev Institute of Petrochemical Synthesis) reported the steam reforming of methanol in the presence of copper-containing catalysts. This reaction has been intensively studied recently in connection with its possible use for hydrogen production (for instance, in fuel cells).

A. Katz *et al.* (University of California at Berkeley, USA) reported an interesting catalyst of a new type. They used calixarenes for obtaining immobilized catalysts. These are cyclic molecules obtained by the condensation of phenol and formaldehyde and have the form of a calyx. Such molecules can form host–guest complexes with neutral molecules and cations. Calixarene immobilized on SiO_2 selectively interacts with aromatic molecules in aqueous solutions. The introduction of Ti or Cu into a calixarene matrix makes it possible to obtain new catalysts (for instance, for the stereoselective epoxidation of olefins and phenol).

V.M. Frolov (Topchiev Institute of Petrochemical Synthesis) reported new data on the synthesis of highly active catalysts for CO_2 methanation based on the complexes of Ru, Rh, and Pt with trioctylamine supported on SiO_2 and Al_2O_3. At relatively low temperatures (130–200°C) the catalyst activity characterized by the turnover frequency is considerably higher than the activity of conventional catalyst prepared by impregnation.

VARIOUS MECHANISTIC STUDIES

The lecture by V.B. Kazanskii (Zelinskii Institute of Organic Chemistry) was devoted to the localization of bivalent cations in ZSM-5 zeolites whose unusual catalytic properties were noted by several researchers. To obtain a zeolite with bivalent cations, an unusual procedure of zeolite treatment in the vapor of metal (Zn), which exchanges with proton, was proposed. Thus, water was excluded from the preparation of ZnZSM-5 zeolites. The structures formed were studied by IR spectroscopy with molecular probes (H_2). It was shown that bivalent Zn, Co, and Ni cations in ZSM-5 are localized near two negatively charged aluminum–oxygen tetrahedrons, which are separated by a single silicon atom. The Zn^{2+} ions with partially compensated positive charge possess Lewis acid properties.

B.L. Trout (MIT, USA) reported the results of a molecular dynamics study of the mechanisms of reactions catalyzed by zeolites. The mechanism of C–C bond formation was studied in most detail in the methanol to olefins (Mobile) process over chabazite. It was found that the reaction $2CH_3OH \longrightarrow C_2H_5OH + H_2O$ occurs in two steps via stable intermediate compounds. In addition to these steps, there are two steps with proton transfer and charge transfer.

B.L. Trout also reported theoretical DFT study of the states of S, O, SO_2, SO_3, and SO_4 species chemisorbed on the Pt(111) surface. The coordination of the species and reactions on the surface strongly depended on the surface coverage and were different at low, intermediate and high coverages. The oxidation of SO_2 was studied using preadsorbed oxygen.

D.V. Besedin (Department of Chemistry, Moscow State University) also applied the DFT method to elucidate the mechanism of C–C hydrogenolysis in alkanes on zirconium hydride supported on SiO_2. E.A. Fushman (Semenov Institute of Chemical Physics) described the effect of water on the catalytic properties of Cp_2TiCl_2/AlR_2Cl in olefin polymerization.

The applications of molecular beams, FEM, and work function measurements allowed V.V. Gorodetskii (Boreskov Institute of Catalysis) to study the mechanism of CO oxidation on Pd(111), Pd(110), and Pd tip surfaces. The low-temperature oxidation was accompanied by reversible transitions between adsorbed and subsurface oxygen. As a result, dissipative structures are observed: oscillations, surface waves, and hysteresis phenomena.

V.Yu. Borovkov *et al.* (Zelinskii Institute of Organic Chemistry and University of Pittsburgh, USA) reported the results of the FTIR study of the electron state of Pt/Al_2O_3 and $(Pt–Cu)/Al_2O_3$. To study the isotopic shifts, mixtures of $^{13}C^{16}O + ^{12}C^{16}O$ were used instead of the conventional $^{13}C^{18}O + ^{12}C^{16}O$ mixture.

P.Yu. Storozhev *et al.* (Institute of Physics of St. Petersburg State University and Universidad de las Islas Baleares, Palma de Mallorca, Spain) carried out a FTIR study of the so-called steric excitations on the surface. This term refers to the adsorption complexes with an unusual geometry and excess energy. Using CO adsorption on cation-exchanged zeolites as an example, the authors showed that CO may bind to a cation through a carbon or an oxygen atom. The study of the temperature dependence of the spectrum provides information on the excitation energy. Such steric excitation was also observed in the course of adsorption of other diatomic and polyatomic molecules and even in HD adsorption.

M.Yu. Kislyuk (Semenov Institute of Chemical Physics) reported on anomalous oxygen desorption from tungsten. Deviations from the classical kinetic theory were explained by the lateral interactions of adjacent oxygen atoms and by the migration of surface oxygen atoms.

V.M. Kogan (Zelinskii institute of Organic Chemistry) presented the results of a comprehensive radioisotopic (^{35}S) study of the sulfided Co–Mo and Ni–Mo catalysts in the hydrodesulfurization reaction. This study made it possible to create a map of active sites on the surface and approach the rational selection of the catalysts for hydrodesulfurization of various heavy oil fractions.

A.M. Volodin *et al.* (Boreskov Institute of Catalysis and Kansas State University, USA) showed that alkali earth oxides (MgO and others) obtained by the sol–gel method have a particle size of 4–8 nm. Using the ESR method, the authors showed that unusual properties of these substances are due to the high concentration of various defects and active sites with low coordination.

I.Z. Ismagilov *et al.* (Boreskov Institute of Catalysis) applied ESR and UV–VIS spectroscopy to study the formation of a Mo–HZSM-5 catalyst for nonoxidative dehydroaromatization of methane. Initial Mo^{6+} reduces to Mo^{5+} through reduction by methane and forms alkylmolybdenum complexes and then carbide-like compounds.

E.M. Sul'man (Tver Engineering University) reported the mechanism of the action of monometallic (Pd) and bimetallic (Pd–Au) catalysts supported on block-copolymer micelles in the reaction of acetylenic alcohol hydrogenation. The FTIR and XPS study of CO adsorption showed that the active sites (Pd atoms) have uniform properties. The addition of gold affects the electron properties and the geometry of active sites.

APPLIED PROBLEMS

A report of many authors delivered by V.A. Sadykov (Boreskov Institute of Catalysis) presented the results of the study of selective NO_x reduction by hydrocarbons in excess oxygen on catalysts based on microporous zirconia pillared clays. Many physical methods were applied in this work. Active sites were characterized by CO and NO adsorption. A number of cations and cation clusters with unusual coordination were found to react with CO and NO. Catalytic properties are studied in the reactions of selective NO_x reduction by propane, propylene, and decane in excess O_2.

A.A. Khasin *et al.* (Boreskov Institute of Catalysis) presented a new concept of the catalyst for Fischer–Tropsch synthesis based on the permeable composite monolith. The latter is a monoporous composite particle with pores ranging from 2 to 20 nm. The high intensity of gas–liquid exchange provided the high efficiency of the process. Diffusion limitations correlate with the size distribution of pores. Methods have been developed for controlling the sizes of pores at the stage of catalyst preparation. The productivity and selectivity depend heavily on the shapes and sizes of particles.

A.S. Lermontov *et al.* (Moscow State University, Department of Chemistry) reported a method for express testing of cobalt-based Fischer–Tropsch catalysts. The method is based on magnetic measurements in the course of temperature-programmed oxidation and reduction.

The talk by V.V. Chesnokov *et al.* (Boreskov Institute of Catalysis and Kansas State University, USA) was devoted to the selective oxidative dehydrogenation of butane to butadiene in the presence of iodine on nanocrystalline MgO, Al_2O_3, and VO_x/MgO catalysts. The addition of molecular iodine shifts the equilibrium toward the products and enables a high selectivity to butadiene at a high conversion of butane. In excess oxygen iodine is completely regenerated and can be returned to the cycle. On the 10% V/MgO catalyst in the presence of 0.25 vol % I_2, the selectivity to C_4H_6 is as high as 57% and the conversion of butane is 56%.

B.N. Kuznetsov *et al.* (Institute of Chemistry and Chemical Engineering, Krasnoyarsk, and Institute of Physical Organic Chemistry and Coal Chemistry, Donetsk) presented the results of the study of the structure, texture, and catalytic properties of palladium catalysts supported on porous carbon materials, chemically modified anthracene and graphite. These studies were carried out using liquid-phase cyclohexane dehydrogenation as a model reaction. The activity of the Pd/graphite and Pd/anthracene catalysts depended on the pore structure of the support and on the size, structure, and distribution of Pd particles.

N.V. Semikolenova (Boreskov Institute of Catalysis) reported the preparation of supported catalysts for ethylene polymerization by the interaction of 2,6-bis[1-(2,6-dimethyldiphenylamino)-ethyl]pyridine–iron(II) ($LFeCl_2$) with the oxide support (SiO_2 or Al_2O_3). Using the method of polymerization quenching by ^{14}CO, the number of active sites and the values of the rate constant of growth in ethylene polymerization on supported $LFeCl_2/SiO_2$ catalyst and in the homogeneous $LFeCl_2$ + (*iso*-Bu)$_3$Al system were determined.

Interesting studies of new catalytic reactions and catalysts and the mechanism of catalysis were also presented at a poster session.

To conclude, I would like to note that the Russian–American Seminar on Catalysis was undoubtedly successful. The seminar organizers selected interesting reports, in most cases of high scientific level. Not all of the catalysis problems were discussed at the seminar. For instance the problems of catalysis in oil refining and gas processing were not discussed while considerable attention was given to the processes of oxidation, however, it is difficult to reach a balance when organizing such a meeting. A drawback of the seminar was that very few American scientists participated in the actual work of the seminar.